PB-232 527

EVALUATION OF EQUATIONS FOR DESIGNING AMMONIACAL SCRUBBERS TO REMOVE SULFUR OXIDES FROM WASTE GAS

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Research Triangle Park, North Carolina

January 1974

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TECHNICAL REPORT DATA
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1. REPORT NO.	2.	3. R
EPA-650/2-74-035		PB 232 527

4. TITLE AND SUBTITLE	5. REPORT DATE
Evaluation of Equations for Designing Ammoniacal Scrubbers to Remove Sulfur Oxides from Waste Gas	January 1974
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
L. I. Griffin	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
EPA, ORD, NERC-RTP Control Systems Laboratory Gas Cleaning and Metallurgical Processes Branch Research Triangle Park, NC 27711	1AB013; ROAP 21ACX-60
	11. CONTRACT/GRANT NO.
	NA--In-house Report
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
NA--In-house Report	Final
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The report reviews the work of H. F. Johnstone in 1935 and of B. A. Chertkov in the 1950's, related to laboratory vapor pressure-temperature measurements of sulfur dioxide, ammonia, and water above ammoniacal solutions. It indicates that, although Johnstone and Chertkov are in general agreement, their measurements lead to different conclusions in several instances. The report suggests resolutions of the differences noted: the relationship recommended should provide a reliable basis for designing ammoniacal scrubbers for removing sulfur oxides from waste gas. As for other absorbents, design data for ammoniacal scrubbers must include detailed knowledge of solution properties. Ammonium sulfite and bisulfite are far more soluble in water than other sulfites. This constitutes an important scrubber credit that has prompted careful study of ammoniacal solutions.

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Vapor Pressure	Air Pollution Control	13B
Ammonium Compounds	Sulfur Oxides	Stationary Sources	7B, 7C
Scrubbers	Ammonia	Ammoniacal Solutions	7A
Desulfurization	Water	H. F. Johnstone	7D
Exhaust Gases		B. A. Chertkov	21B
Flue Gases			
Measurement			14B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Unlimited	Unclassified	24
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	$4.25

EPA Form 2220-1 (9-73)

EPA-650/2-74-035

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ROAP No. 21ACX-60
Program Element No. 1AB013

Prepared for

NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N. C. 27711

January 1974

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INTRODUCTION

Scrubbing waste gas with ammoniacal solutions for removing sulfur oxides has been practiced commercially in the United States, Canada, Russia, Japan, Czechoslovakia and Romania during the last several decades. These limited operations of varying duration were prompted by serious local air pollution problems. In several instances, scrubbing was discontinued when the processing operations were modified to reduce pollution or when a cleaner fuel was supplied.

In recent years, interest in air pollution has been intensified on a national and international scale. Ammonia scrubbing has many potential advantages over competing waste gas cleaning processes. This is particularly true if improvements expected are convincingly demonstrated. Since the properties of ammoniacal solutions have received considerable attention and careful laboratory measurements have been made, a number of the tools needed for process improvements studies are available in the literature. For example, H.F. Johnstone and coworkers at the University of Illinois in the 1930's published vapor pressure data for ammonia, sulfur dioxide, and water above ammoniacal solutions along with the solution pH's. And, in the 1950's, B.A. Chertkov and his Russian countrymen reviewed and repeated much of Johnstone's work.

The purpose of this paper is to comment on the accuracy and limitations of the data obtained by both investigators, and to recast Johnstone's vapor pressure equations so that they can be used more easily in designing and controlling ammonia scrubbing processes for removing sulfur oxides from waste gas.

JOHNSTONE'S STUDIES

H. F. Johnstone's interest in controlling air pollution was demonstrated by his extensive work on a number of processes for scrubbing sulfur oxides from waste gases. Ammoniacal scrubbing, among the first processes considered by Johnstone, was studied very carefully and completely. In preparation for this work, Johnstone[1] measured the vapor pressure of ammonia, sulfur dioxide, and water above ammoniacal solutions of varying compositions and pH's. As he surmised, vapor pressures were found to be functions of temperature and composition while solution pH was a function of composition alone. Theoretical considerations served as the basis of Johnstone's correlations of his experimental vapor pressure data. These considerations are discussed carefully in Johnstone's paper and will not be repeated here. While Johnstone's pH-composition relationship is empirical, it is also plausible and appealingly simple. And, the degree of correlation is quite good.

The equations used by Johnstone to correlate vapor pressures that he measured are summarized below.

$$VP_{SO_2} = M \frac{(2S - C + nA)^2}{C - S - nA} \qquad (1)$$

$$VP_{NH_3} = N \frac{C\,(C - S - nA)}{2S - C + nA} \qquad (2)$$

$$VP_{H_2O} = VP_w \frac{100}{100 + C + S + A} \qquad (3)$$

VP_{SO_2}, VP_{NH_3}, VP_{H_2O} are vapor pressures of the indicated compounds, in millimeters of mercury, above ammoniacal solutions.

VP_w is the vapor pressure of pure water at the temperature of the ammoniacal solution. VP_w is in millimeters of mercury.

M and N are coefficients relating the vapor pressures to solution temperature. As solution temperature increases, the respective vapor pressures increase in response to increasing values of M and N.

Solution composition is defined by the following ratios.

S = mols of SO_2 per 100 mols of H_2O.

C = mols of NH_3 per 100 mols of H_2O.

C_a = C-nA. For solutions in which a strong acid is present, which may be considered as completely ionized, such as sulfuric acid, n and A are defined as

n = valence of acid ion

A = mols of strong acid per 100 mols of H_2O

Since composition in all cases is referred to 100 mols of water, it is prudent to inquire whether the water referred to is uncombined or "free" water or whether it is total water including the water of constitution. According to Johnstone, the equations he used in correlating vapor pressure data are based on total water including water of constitution. The difference in calculated composition ratios when "free" and total water are used can be significant as shown below.

Compounds Contained in Solution	Composition of Solution Determined Analytically, Mols	Mols Contained in Indicated Compound			
		NH_3	SO_2	$SO_4^=$	H_2O
$(NH_4)_2SO_4$	1	2	--	1	1
$(NH_4)_2SO_3$	2	4	2	--	2
NH_4HSO_3	6	6	6	--	6
"Free" H_2O	91	--	--	--	91
TOTAL	100	12	8	1	100

Composition Ratios	Composition Ratios Referenced to "Free" Water	Total Water
S	8.79	8.00
C	13.19	12.00
A	1.10	1.00
C_a	10.99	10.00

B.A. Chertkov, whose work is referred to later, employed Johnstone's composition ratios and equations as well as another system for expressing composition. To avoid confusion, composition ratios as defined by Johnstone will be used exclusively throughout this report. And, it should be remembered that Johnstone's composition ratios are referenced to <u>total</u> water.

As noted earlier, the vapor pressure of both SO_2 and NH_3 above ammoniacal solutions increases with increasing solution temperature. The coefficients, M and N - see Equations 1 and 2 - are related to solution temperature through the following equations.

$$\log_{10} M = 5.865-2369/T \qquad (4)$$

$$\log_{10} N = 13.680-4987/T \qquad (5)$$

In the above expressions, T is expressed in degrees Kelvin. Values of M and N are listed in Table 1 for $1^{o}F$ increments ranging from 115 to $145^{o}F$. For this range, M doubles when the temperature is increased by $24^{o}F$, and N doubles when the temperature is increased by $12^{o}F$.

Johnstone notes that "some variations in the values of M and N are to be expected as the total salt concentration is changed." However, for the broad range of concentrations studied by Johnstone, "a single value for each of the constants at any one temperature will reproduce the actual vapor pressures within 10 percent."

Johnstone points out that "for the concentration range in which we are interested and for the pH range between 4.5 and 6, it is permissible to make simplifying assumptions" resulting in the composition groupings or expressions functionally related to the vapor pressure of SO_2 and NH_3 - see Equations 1 and 2. Johnstone cautions, however, against using Equations 1 and 2 outside of the pH range listed above "where the ionization of ammonium hydroxide or sulfurous acid, respectively, can not be considered as being complete." After additional related information is discussed, limitations on Equations 1 and 2 will be considered further.

The above discussions have been concerned primarily with the vapor pressures of SO_2 and NH_3 above ammoniacal solutions. In addition, Johnstone measured the vapor pressure of water above ammoniacal solutions.

Johnstone found that the experimentally determined water vapor pressures could be predicted with good accuracy from Raoult's law. He noted that "it is perhaps somewhat surprising that the simple Raoult's law agrees so well with the experimental data." In calculating the vapor pressure of water above ammoniacal solutions containing sulfate, Johnstone used Equation 3. When the solution contains no sulfate, A is zero and Equation 3 reduces to the simplified expression reported by Johnstone.[1]

As noted earlier, Johnstone presented an empirical relationship between the composition of ammoniacal solutions and pH. Discussion of this correlation is being deferred until Chertkov's more complete data on the same subject are presented so that comparisons can be made and more meaningful conclusions reached.

CHERTKOV'S STUDIES

Chertkov,[2] like Johnstone, studied the properties of ammoniacal solutions extensively. Both investigators measured the vapor pressure of sulfur dioxide above artificially prepared solutions containing ammonium sulfite and bisulfite. They found the measured values to be in good agreement with Johnstone's equation based on theoretical considerations. As opposed to artificially prepared solutions, commercial sulfite solutions obtained by scrubbing waste gases contain small percentages of sulfate resulting from oxidation and other causes. If SO_2 is to be released by acidification of the sulfites, oxidation to sulfate should be discouraged so as to maximize the SO_2 recovered. However, since the scrubber solution will inevitably contain some sulfate, both Chertkov and Johnstone measured the vapor pressures of SO_2 above solutions containing sulfite, bisulfite, and sulfate.

Chertkov found the vapor pressure of SO_2 increased significantly when $(NH_4)_2SO_4$ was added to solutions of ammonium sulfites. Chertkov explains this by noting "if $(NH_4)_2SO_4$ -a completely dissociated salt with a common cation is added to an ammonium sulfite-bisulfite solution, the equilibrium for hydrolysis is displaced" toward "undissociated ammonium hydroxide and sulfurous acid." The increased concentrations of undissociated base and acid should "increase the vapor pressure of SO_2 and NH_3 above the solution."

Chertkov "assumed that the increase in SO_2 vapor pressure when sulfate is added (to a sulfate free solution) is proportional to the increase in the total concentration of salt in the solution." He found that the SO_2 vapor pressures he measured above solutions of ammonium sulfites and sulfate could be calculated as the product of two factors. The vapor pressure of SO_2 above solutions of ammonium sulfite, bisulfite, and sulfate is equal to the vapor pressure above sulfate-free solution multiplied by the ratio of total salt concentration after ammonium sulfate addition to the total concentration before addition.

Johnstone, unlike Chertkov, found no statistically significant effect of added ammonium sulfate on the vapor pressure of SO_2 above solutions containing all three salts. This finding is in accord with Equation 1 derived by Johnstone from theoretical considerations. Unfortunately, the SO_2 vapor pressure data obtained by Johnstone and Chertkov above sulfite solutions containing ammonium sulfate do not agree. But the data collected by each investigator are correlated equally well when the appropriate equations are used. In this case, it is necessary to make a choice - and hopefully the correct choice - so that process calculations for air pollution control systems employing ammoniacal solutions will not contain errors from using incorrect vapor

pressure data. In the absence of convincing data, abstract considerations are used in choosing between different procedures for calculating vapor pressures.

A careful consideration of the work of both investigators suggests that Johnstone's studies are more reliable than those reported by Chertkov. Johnstone's vapor pressure equations for both SO_2 and NH_3 were derived from sound theoretical considerations and are limited by solution pH as noted. Chertkov's vapor pressure data are restricted to SO_2; no ammonia vapor pressures are reported. Also, Chertkov's correlation for SO_2 vapor pressure above solutions containing sulfate is empirical with no theoretical foundation. Finally, Chertkov's studies emphasized dilute solutions and solutions containing higher-than-normal ratios of bisulfite to sulfite. These are not conditions of major interest, and the results Chertkov obtained may reflect these atypical conditions.

In addition to vapor pressures above ammoniacal solutions, both Johnstone and Chertkov measured the pH of solutions of sulfite, bisulfite, and sulfate. Johnstone[1] found that "over the entire range of concentrations (he) studied, there is a linear function of the sulfur dioxide-ammonia ratio. The empirical equation

$$pH = 9.2 - 4.62\ (S/C)$$

reproduces the observed values within 0.1 pH unit. Obviously, however, the equation cannot be extrapolated to the bisulfite ratio." It is to be noted that although Johnstone related pH to S/C by the equation reported, his measured pH values of solutions containing sulfate require S/C_a as the correlating ratio. Thus, the relationship

$$pH = 9\ 2 - 4.62\ (S/C_a)$$

is more rigorous and fits all of Johnstone's data. Chertkov also relates pH to S/C_a, and his data are far more extensive than Johnstone's data.

Over the S/C_a range of 0.7 to 0.9, Chertkov[3] found a linear relationship between pH and S/C_a represented by

$$pH = 8.88 - 4.0\ (S/C_a)$$

As may be noted from Figure 1, the linear relationships of both investigators obtained with artificially prepared solutions are in reasonable agreement. Chertkov points out, however, that all the experimental data plotted in Figure 1 "fit reasonably accurately around a curve of a shape characteristic for such determinations-with sharp breaks at critical points corresponding to the appearance of new compounds in solution, in this

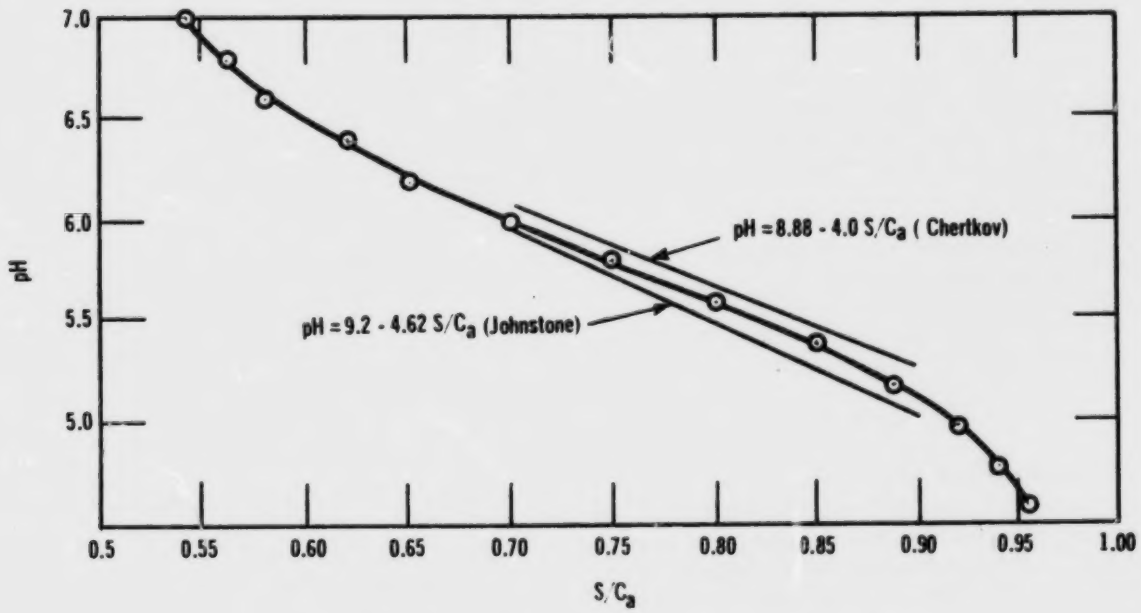

Figure 1. The pH values of ammonium sulfite-bisulfite solutions.

instance at S/C_a =0.5 and S/C_a =1.0." Chertkov notes further that "the presence of fairly large amounts of ammonium sulfate and thiosulfate and small amounts of inhibitor and light ash in the production liquor" - see curve defined by points on Figure 1 -" has virtually no effect on the pH, because of its high buffer effect. The total ammonium sulfite-bisulfite concentration likewise has little practical effect on solution pH."

Thus, both Chertkov and Johnstone agree that acidity or pH of ammoniacal solutions of sulfites and sulfate is a function of S/C_a. The influence of other factors appears to be far less important.

JOHNSTONE'S EQUATIONS RECAST FOR SIMPLICITY

Johnstone's equations for calculating the vapor pressure of SO_2 and NH_3 have been extremely useful in studying ammoniacal scrubbing of waste gases to remove sulfur oxides. Nearly forty years after Johnstone published his vapor pressure equations, they still appear to be the most complete and reliable. Despite wide acceptance of Johnstone's equations, simplified forms of the relationships are desirable. Simplified expressions should expedite use of the equations and indicate by special groupings the specific influence of important variables, e.g., solution acidity, on the individual vapor pressures. This, of course, would provide a better understanding of the vapor pressure equations - a better understanding that might be useful in extending process studies for controlling pollution.

Johnstone's vapor pressure equations for SO_2 and NH_3 given earlier are restated below.

$$VP_{SO_2} = M \frac{(2S-C + nA)^2}{C - S - nA} \qquad (1)$$

$$VP_{NH_3} = N \frac{C(C - S - nA)}{2S - C + nA} \qquad (2)$$

Since A refers to sulfuric acid, in this case n is 2 matching the valence of $SO_4^=$. For this system, Equations 1 and 2 are more specifically defined by:

$$VP_{SO_2} = M \frac{(2S - C + 2A)^2}{C - S - 2A} \qquad (1')$$

$$VP_{NH_3} = N \frac{C(C - S - 2A)}{2S - C + 2A} \qquad (2')$$

The related quantities in Equations 1' and 2' are defined earlier and are defined identically in the recast equations given in Appendix A.

Appendix A shows that Equations 1' and 2' may be expressed as follows.

$$VP_{SO_2} = MSD \qquad (6)$$

$$VP_{NH_3} = NCE \qquad (7)$$

Both D and E are functions of S/C_a.

$$D = \frac{(2S/C_a - 1)^2}{S/C_a\ (1 - S/C_a)} \qquad (8)$$

$$E = \frac{1 - S/C_a}{2S/Ca - 1} \qquad (9)$$

Solution acidity is also a function of S/C_a, hence D and E are referred to as acidity factors in Equations 6 and 7 and Tables 2 and 3. Thus, the vapor pressures of both SO_2 and NH_3 may be calculated as the product of three factors - (1) an appropriate temperature coefficient, multiplied by (2) the solution concentration of the component referred to in the vapor pressure equation, multiplied by (3) an appropriate acidity factor.

Table 1. TEMPERATURE COEFFICIENTS FOR JOHNSTONE'S VAPOR PRESSURE EQUATIONS

Temperature °F	Temperature Coefficients		Temperature °F	Temperature Coefficients	
	M^a	N^b		M^a	N^b
115	0.0279	0.0116	130	0.0430	0.0287
116	0.0287	0.0122	131	0.0443	0.0304
117	0.0296	0.0130	132	0.0455	0.0323
118	0.0304	0.0138	133	0.0468	0.0342
119	0.0314	0.0147	134	0.0481	0.0363
120	0.0323	0.0156	135	0.0495	0.0385
121	0.0332	0.0167	136	0.0509	0.0408
122	0.0342	0.0177	137	0.0523	0.0432
123	0.0352	0.0188	138	0.0538	0.0458
124	0.0363	0.0200	139	0.0553	0.0486
125	0.0373	0.0212	140	0.0568	0.0514
126	0.0384	0.0226	141	0.0584	0.0545
127	0.0395	0.0240	142	0.0600	0.0577
128	0.0407	0.0254	143	0.0616	0.0611
129	0.0418	0.0270	144	0.0633	0.0646
			145	0.0650	0.0684

[a] $\log_{10} M = 5.865 - 2369/T\ ^{o}K$

[b] $\log_{10} N = 13.680 - 4987/T\ ^{o}K$

Table 2. ACIDITY FACTORS FOR JOHNSTONE'S EQUATION FOR VAPOR PRESSURE OF SO_2

	[a]Acidity factor, D									
S/C_a	0	1	2	3	4	5	6	7	8	9
0.57	-	-	-	-	-	-	-	-	0.100	0.102
0.58	0.105	0.108	0.111	0.113	0.116	0.119	0.122	0.125	0.128	0.131
0.59	0.134	0.137	0.140	0.143	0.147	0.150	0.153	0.156	0.160	0.163
0.60	0.167	0.170	0.174	0.177	0.181	0.185	0.188	0.192	0.196	0.200
0.61	0.203	0.207	0.211	0.215	0.219	0.223	0.228	0.232	0.236	0.240
0.62	0.244	0.249	0.253	0.258	0.262	0.267	0.271	0.276	0.281	0.285
0.63	0.290	0.295	0.300	0.305	0.310	0.315	0.320	0.325	0.330	0.335
0.64	0.340	0.346	0.351	0.356	0.362	0.367	0.373	0.378	0.384	0.390
0.65	0.396	0.401	0.407	0.413	0.419	0.425	0.431	0.438	0.444	0.450
0.66	0.456	0.463	0.469	0.476	0.482	0.489	0.496	0.502	0.509	0.516
0.67	0.523	0.530	0.537	0.544	0.551	0.558	0.566	0.573	0.581	0.588
0.68	0.596	0.603	0.611	0.619	0.627	0.634	0.642	0.650	0.659	0.667
0.69	0.675	0.683	0.692	0.700	0.709	0.718	0.726	0.735	0.744	0.753
0.70	0.762	0.771	0.780	0.789	0.799	0.808	0.818	0.827	0.837	0.847
0.71	0.857	0.867	0.877	0.887	0.897	0.907	0.918	0.928	0.939	0.950
0.72	0.960	0.971	0.982	0.993	1.004	1.016	1.027	1.039	1.050	1.062
0.73	1.074	1.085	1.097	1.110	1.122	1.134	1.147	1.159	1.172	1.185
0.74	1.198	1.211	1.224	1.237	1.250	1.264	1.277	1.291	1.305	1.319
0.75	1.333	1.348	1.362	1.377	1.391	1.406	1.421	1.436	1.451	1.467
0.76	1.482	1.498	1.514	1.530	1.546	1.563	1.579	1.596	1.612	1.629
0.77	1.647	1.664	1.681	1.699	1.717	1.735	1.753	1.771	1.790	1.809
0.78	1.828	1.847	1.866	1.885	1.905	1.925	1.945	1.965	1.986	2.007
0.79	2.028	2.049	2.070	2.092	2.114	2.136	2.158	2.181	2.204	2.227
0.80	2.250	2.274	2.297	2.321	2.346	2.370	2.395	2.421	2.446	2.472
0.81	2.498	2.524	2.551	2.578	2.605	2.632	2.660	2.688	2.717	2.746
0.82	2.775	2.805	2.835	2.865	2.895	2.926	2.958	2.990	3.022	3.054
0.83	3.087	3.121	3.154	3.189	3.223	3.258	3.294	3.330	3.366	3.403
0.84	3.440	3.478	3.517	3.556	3.595	3.635	3.676	3.717	3.758	3.800
0.85	3.843	3.887	3.930	3.975	4.020	4.066	4.113	4.160	4.208	4.256
0.86	4.306	4.356	4.406	4.458	4.510	4.563	4.617	4.672	4.728	4.784
0.87	4.842	4.900	4.959	5.019	5.081	5.143	5.206	5.270	5.336	5.402
0.88	5.470	5.538	5.608	5.680	5.752	5.826	5.901	5.977	6.055	6.134
0.89	6.215	6.297	6.380	6.466	6.553	6.641	6.731	6.824	6.918	7.013
0.90	7.111	7.211	7.313	7.417	7.523	7.631	7.742	7.855	7.971	8.089
0.91	8.210	8.334	8.460	8.590	8.722	8.858	8.996	9.139	9.284	9.434
0.92	9.587	9.744	9.905	-	-	-	-	-	-	-

[a]Acidity factor, $D = \frac{(2S/C_a - 1)^2}{S/C_a(1 - S/C_a)}$

Table 3. ACIDITY FACTORS FOR JOHNSTONE'S EQUATION FOR VAPOR PRESSURE OF NH_3

	[a]Acidity factor, E									
S/C_a	0	1	2	3	4	5	6	7	8	9
0.52	-	-	-	-	9.917	9.500	9.115	8.759	8.429	8.121
0.53	7.833	7.565	7.313	7.076	6.853	6.643	6.444	6.257	6.079	5.910
0.54	5.750	5.598	5.452	5.314	5.182	5.056	4.935	4.819	4.708	4.602
0.55	4.500	4.402	4.308	4.217	4.130	4.045	3.964	3.886	3.810	3.737
0.56	3.667	3.598	3.532	3.468	3.406	3.346	3.288	3.231	3.176	3.123
0.57	3.071	3.021	2.972	2.925	2.878	2.833	2.789	2.747	2.705	2.665
0.58	2.625	2.586	2.549	2.512	2.476	2.441	2.407	2.374	2.341	2.309
0.59	2.278	2.247	2.217	2.188	2.160	2.132	2.104	2.077	2.051	2.025
0.60	2.000	1.975	1.951	1.927	1.904	1.881	1.858	1.836	1.815	1.794
0.61	1.773	1.752	1.732	1.712	1.693	1.674	1.655	1.637	1.619	1.601
0.62	1.583	1.566	1.549	1.533	1.516	1.500	1.484	1.469	1.453	1.438
0.63	1.423	1.408	1.394	1.380	1.366	1.352	1.338	1.325	1.312	1.299
0.64	1.286	1.273	1.261	1.248	1.236	1.224	1.212	1.201	1.189	1.178
0.65	1.167	1.156	1.145	1.134	1.123	1.113	1.103	1.092	1.082	1.072
0.66	1.063	1.053	1.043	1.034	1.024	1.015	1.006	0.997	0.988	0.979
0.67	0.971	0.962	0.953	0.945	0.937	0.929	0.920	0.912	0.904	0.897
0.68	0.889	0.881	0.874	0.866	0.859	0.851	0.844	0.837	0.830	0.823
0.69	0.816	0.809	0.802	0.795	0.789	0.782	0.776	0.769	0.763	0.756
0.70	0.750	0.744	0.738	0.732	0.725	0.720	0.714	0.708	0.702	0.696
0.71	0.690	0.685	0.679	0.674	0.668	0.663	0.657	0.652	0.647	0.642
0.72	0.636	0.631	0.626	0.621	0.616	0.611	0.606	0.601	0.596	0.592
0.73	0.587	0.582	0.578	0.573	0.568	0.564	0.559	0.555	0.550	0.546
0.74	0.542	0.537	0.533	0.529	0.525	0.520	0.516	0.512	0.508	0.504
0.75	0.500	0.496	0.492	0.488	0.484	0.480	0.477	0.473	0.469	0.465
0.76	0.462	0.458	0.454	0.451	0.447	0.443	0.440	0.436	0.433	0.429
0.77	0.426	0.423	0.419	0.416	0.412	0.409	0.406	0.403	0.399	0.396
0.78	0.393	0.390	0.387	0.383	0.380	0.377	0.374	0.371	0.368	0.365
0.79	0.362	0.359	0.356	0.353	0.350	0.347	0.345	0.342	0.339	0.336
0.80	0.333	0.331	0.328	0.325	0.322	0.320	0.317	0.314	0.312	0.309
0.81	0.306	0.304	0.301	0.299	0.296	0.294	0.291	0.289	0.286	0.284
0.82	0.281	0.279	0.276	0.274	0.272	0.269	0.267	0.265	0.262	0.260
0.83	0.258	0.255	0.253	0.251	0.249	0.246	0.244	0.242	0.240	0.237
0.84	0.235	0.233	0.231	0.229	0.227	0.225	0.223	0.220	0.218	0.216
0.85	0.214	0.212	0.210	0.208	0.206	0.204	0.202	0.200	0.198	0.196
0.86	0.194	0.193	0.191	0.189	0.187	0.185	0.183	0.181	0.179	0.178
0.87	0.176	0.174	0.172	0.170	0.168	0.167	0.165	0.163	0.161	0.160
0.88	0.158	0.156	0.154	0.153	0.151	0.149	0.148	0.146	0.144	0.143
0.89	0.141	0.139	0.138	0.136	0.135	0.133	0.131	0.130	0.128	0.127
0.90	0.125	0.123	0.122	0.120	0.119	0.117	0.116	0.114	0.113	0.111
0.91	0.110	0.108	0.107	0.105	0.104	0.102	0.101	0.100	-	-

[a]Acidity factor, $E = \frac{1 - S/C_a}{2S/C_a - 1}$

LIMITATIONS OF JOHNSTONE'S VAPOR PRESSURE EQUATIONS

According to Johnstone, his vapor pressure equations for SO_2 and NH_3 should not be used outside the pH range of 4.5 to 6.0. At lower and higher pH's, Johnstone notes that some of the assumptions made in deriving the equations are no longer valid and the accuracy of the equations is less reliable. Johnstone's equations, as recast in Appendix A, show that vapor pressures of SO_2 and NH_3 are functions of solution temperature, concentration of SO_2 and NH_3 in solution, and S/C_a. While pH is primarily a function of S/C_a, other factors exert a small influence. Thus, different investigators obtain slightly different relationships between pH and S/C_a, e.g., Johnstone and Chertkov - See Figure 1. If Johnstone's relationship between pH and S/C_a is valid, a pH of 6.1 (only 0.1 pH unit higher than the upper pH limit recommended) is consistent with a S/C_a value of 0.67. While this S/C_a should be acceptable, the accuracy of calculated vapor pressure for lower values of S/C_a and higher pH's will be more questionable.

While Johnstone's vapor pressure equations should be reliable within the pH range of 4.5 to 6.0, R.A. Berdyanskaya and coworkers[4] found that accurate SO_2 vapor pressures could not be calculated from Johnstone's equation when S/C_a is above 0.87. According to Berdyanskaya, "the simplified equation for calculating the equilibrium partial pressure of SO_2 over ammonium sulfite-bisulfite solution, proposed by Johnstone, gives large errors when applied to solutions in which more than 85% of the dissolved SO_2 is bound in the form of bisulfite ($\underline{S/C} > 0.87$), especially at temperatures over 80°." But, according to Johnstone, the upper limit on S/C_a should be well above 0.87. Nevertheless, the more restrictive upper limitation on S/C_a of 0.87 is recommended in calculating SO_2 vapor pressures. While this more conservative limitation on S/C_a may not be entirely justified, it imposes few, if any, practical limitations on development of waste gas scrubbing processes employing ammoniacal solutions.

In summary, vapor pressures for SO_2 and NH_3 calculated from Johnstone's equations are more reliable when the acidity factors lie within the S/C_a range of 0.67 to 0.87. Outside this range, the acidity factors are more questionable, and the vapor pressures are less reliable.

APPLICATION OF JOHNSTONE'S RECAST EQUATIONS

As noted earlier, Johnstone's vapor pressure equations in recast simplified form provide a better understanding of the factors controlling the vapor pressures so that process results may be optimized. Secondly, the recast equations expedite vapor pressure calculations. Process optimization calculations using the recast equations are outside the scope of this report; however, an example of calculations using the simplified vapor pressure equations is outlined below.

Consider the top stage of an ammoniacal scrubber to remove SO_2 from waste gas. If vapor-liquid equilibrium is established and 200 ppm of SO_2 escape with the waste gas, calculate S, C_a, and C in the top stage liquor and the ammonia loss in ppm in the waste gas. Assume the following conditions prevail in the top stage.

Conditions

Temperature, ^oF = 130

S/C_a = 0.75

A = 0.1S

Calculations for the Example

VP_{SO_2} = MSD

VP_{SO_2} = 200 ppm = 0.152mm of Hg

M at 130^oF = 0.0430 See Table 1

D for 0.75 S/C_a = 1.333 See Table 2

$$S = \frac{0.152}{0.0430 \times 1.333} = 2.65$$

S/C_a = 0.75

C_a = S/0.75 = 2.65/0.75 = 3.533

A = 0.1S = 0.1 X 2.65 = 0.265

$C = C_a + 2A = 3.533 + 2 \times 0.265 = 4.063$

VP_{NH_3}	=	NCE	
N at 130°F	=	0.0287	See Table 1
C	=	4.063	
E for 0.75 S/C_a	=	0.500	See Table 3
VP_{NH_3}	=	0.0287 X 4.063 X 0.500	
	=	0.0583 mm of Hg = 76.7 ppm	

Calculation of the example using Johnstone's equations in their original form is considerably more time consuming than the simplified procedure outlined above.

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APPENDIX A

JOHNSTONE'S RECAST VAPOR PRESSURE EQUATIONS

$$VP_{SO_2}(\text{mm}) = M \frac{(2S - C + 2A)^2}{C - S - 2A} \qquad (1')$$

$$= M \frac{(2S - C_a)^2}{C_a - S}$$

$$= M \frac{4S^2 - 4SC_a + C_a^2}{C_a - S}$$

$$= M \frac{C_a^2(4S^2/C_a^2 - 4S/C_a + 1)}{C_a(1 - S/C_a)}$$

$$= M \frac{C_a(2S/C_a - 1)^2}{1 - S/C_a}$$

$$= M \frac{(S/C_a)(C_a)(2S/C_a - 1)^2}{S/C_a(1 - S/C_a)}$$

$$= MS \frac{(2S/C_a - 1)^2}{S/C_a(1 - S/C_a)}$$

$$= MSD \qquad (6)$$

$$VP_{NH_3}(\text{mm}) = N \frac{C(C - S - 2A)}{2S - C + 2A} \qquad (2')$$

$$= NC \frac{C_a - S}{2S - C_a}$$

$$= NC \frac{C_a(1 - S/C_a)}{C_a(2S/C_a - 1)}$$

$$= NC \frac{1 - S/C_a}{2S/C_a - 1}$$

$$= NCE \qquad (7)$$